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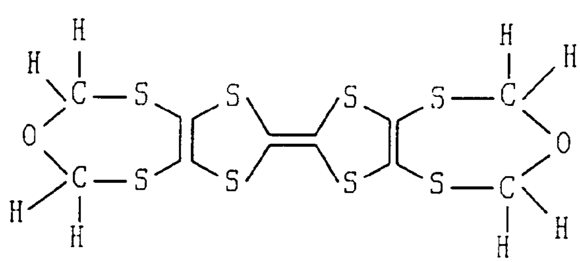
(54) Organic charge transfer complex.

(57) An organic charge transfer complex comprising an electron donor and an electron acceptor, the electron donor is at least one of bis(oxapropylenedithio)tetrathiafulvalene represented by formula (1):



(1)

and bis(thiapropylenedithio)tetrathiafulvalene represented by formula (2):

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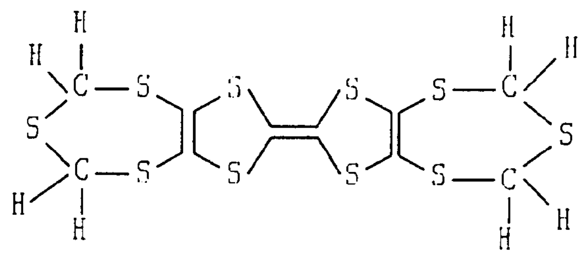


(2)

FIELD OF THE INVENTION

The present invention relates to an organic charge transfer complex, and more particularly to an organic charge transfer complex which is expected to be applied to organic electrically conductive materials, organic superconductive materials, organic magnetic substances, organic electrochromic materials, and organic electroluminescent materials.

BACKGROUND OF THE INVENTION

Compounds which are expected to be applied to the above-described fields, such as organic electrically conductive materials, organic superconductive materials, organic magnetic substances, organic electrochromic materials, and organic electroluminescent materials, include an organic charge transfer complex comprising an electron donors (donor molecule) and an electron acceptor (acceptor molecule or anion), as described in "TTF-TCNQ Complexes and Related Materials", (written by Gunji Saito and Kunihiko Yamaji) in The Elements of Chemistry, No. 42, (Chemistry of Conductive Low Dimensional Materials) (1983) edited by Chemical Society of Japan, published by the publishing Gakkai Shuppan Center, Japan.

Examples of the conventional donor molecules include compounds having a fulvalene skeleton such as tetrathiafulvalene (TTF), tetramethyltetraselenafulvalene (TMTSF), and bisethylenedithiatetrathiafulvalene (BEDT-TTF). Examples of the conventional acceptor molecules include tetracyanoquinodimethane (TCNQ). Examples of the conventional anions include hexafluorophosphate anion (PF_6^-), perchlorate anion (ClO_4^-) and triiodide anion (I_3^-).

Typical examples of the conventional organic charge transfer complexes include electrically conductive complexes such as TTF-TCNQ (σ_{RT} = 500 s/cm) and TMTSF-TCNQ (σ_{RT} = 800 s/cm) and superconductive complexes such as $(TMTSF)_2ClO_4$ (critical temperature Tc = 1.4 K), β-$(BEDT\text{-}TTF)_2I_3$ (Tc = 8 K), χ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ (Tc = 10.4 K) and χ-$(BEDT\text{-}TTF)_2Cu(N(CN)_2)Cl$ (Tc = 13 K).

However, any of the conductive complexes that are put to practical use at present has a problem in that anisotropy in electrical conductance is high. Further, among the superconductive complexes that are put to practical use at present, the compound having the highest critical temperature is the above-described χ-$(BEDT\text{-}TTF)_2Cu(N(CN)_2)Cl$ having Tc = 13 K, and any compound having a critical temperature higher than that described above cannot be obtained at present.

Accordingly, it is demanded to develop novel complexes having characteristics which conventional complexes do not possess, such as conductive complexes having low anisotropy in electrical conductivity, superconductive complexes having a higher critical temperature, and complexes having excellent characteristics as semiconductors.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide an organic charge transfer complex which is free from the problems associated with the prior art.

Another object of the present invention is to provide conductive complexes having low anisotropy in electrical conductivity, superconductive complexes having a higher critical temperature, and complexes having excellent characteristics as semiconductors.

Other objects and effects of the present invention will be apparent from the following description.

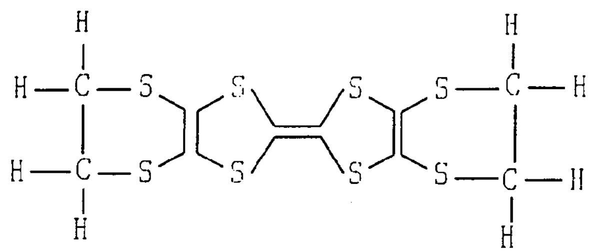
The present inventors have made an analysis of electric conduction mechanisms of organic charge transfer complexes comprising donor molecules having a fulvalene skeleton which are put to practical use at present. As a result, they have found that anisotropy in electrical conductivity is caused by the crystal structures of the organic charge transfer complexes.

It is known that general organic charge transfer complexes have a separate laminate type crystal structure, in which a donor molecule and an acceptor molecule or an anion stand in separate lines to form separate columns, respectively. The donor molecule having a fulvalene skeleton is arranged so that the planar fulvalene skeleton is put parallel within the column.

Charge migrates from the donor molecule to the acceptor molecule or the anion, and a carrier generated on the column of the donor molecule migrates through the crystal along the molecular orbital spreading in the direction of the column. As a result, electrical conductivity is developed. The donor molecule having a fulvalene skeleton had such a tendency that its molecular orbital spreads one-dimensionally or two-dimensionally, and therefore anisotropy in electrical conductivity is produced.

In the case of BEDT-TTF represented by formula (3), such molecular orbital as described above is apt to spread two-dimensionally. Therefore, when BEDT-TTF is used in combination with an anion, a laminar

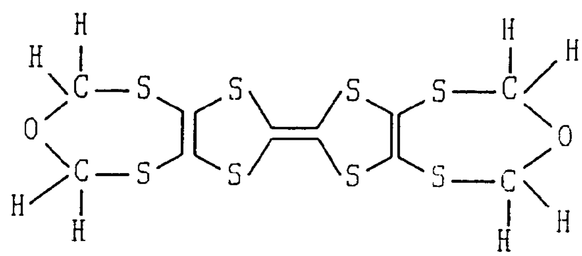
two-dimensional structure composed of a donor layer and an anion layer is formed, the interaction of the donor layers is reduced by the effect of the anion layer adjacent thereto, and anisotropy in electrical conductance is thus further increased.



(3)

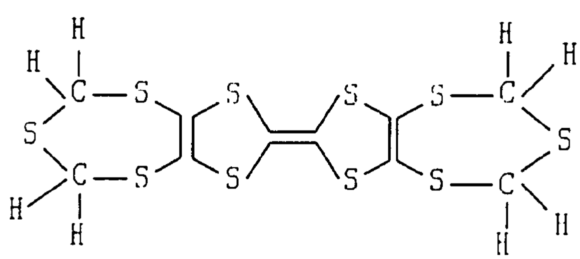
The present inventors have made studies on the molecular orbital of the BEDT-TTF molecule, and have found that when an oxygen atom or a sulfur atom is introduced into the ethylene group positioned near the anion, the spreading of the molecular orbital in the direction perpendicular to the in-plane direction of the donor layer is increased, and the molecular orbital has three-dimensional spreading, and at the same time, the interaction of the donor layers is increased and as a result, the anisotropy in electrical conductivity can be canceled. Further, the present inventors have found that when anisotropy in electrical conductivity is canceled, the electrical conductivity of the organic charge transfer complexes can be improved, and there is a possibility that superconductive complexes having a critical temperature higher than that of χ-(BEDT-TTF)$_2$Cu(N(CN)$_2$)Cl (Tc = 13 K) can be obtained and complexes having excellent characteristics as semiconductors can be obtained.

The present invention provides an organic charge transfer complex comprising an electron donor and an electron acceptor, the electron donor is at least one of bis(oxapropylenedithio)tetrathiafulvalene (hereinafter referred to as BOPDT-TTF) represented by formula (1):



(1)

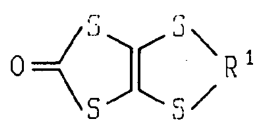
and bis(thiapropylenedithio)tetrathiafulvalene (hereinafter referred to as BTPDT-TTF) represented by formula (2):



(2)

DETAILED DESCRIPTION OF THE INVENTION

BOPDT-TTF of formula (1) and BTPDT-TTF of formula (2) can be synthesized by various synthesis methods. In a preferred embodiment, a precursor represented by formula (4):



(4)

(wherein R^1 represents $-CH_2-O-CH_2-$ or $-CH_2-S-CH_2-$) is heated in the presence of a trialkyl phosphite with stirring to couple two molecules, thereby synthesizing the compound. This method is preferred from the standpoint of production efficiency and safety.

The precursor of formula (4) can be synthesized by various methods. In a preferred embodiment, 1,3,4,6-tetrathiapentalene-2,5-dione is reacted in an alcohol solution containing a methoxide of an alkaline metal under an inert atmosphere at a temperature of 30 ° C or lower, to selectively open one of its rings, thereby producing 1,3-dithiol-2-one-4,5-dithiolate dianion, which is then reacted with a compound containing a divalent organic group corresponding to the group R^1 in formula (4). This method is preferred from the standpoint of production efficiency and safety.

The electron acceptor which can be used in combination with the above BOPDT-TTF and/or BTPDT-TTF is not particularly limited and includes conventional acceptor molecules and anions. Examples of the acceptor molecules include tetracyanoquinodimethanes such as tetracyanoquinodimethane (TCNQ) and derivatives thereof; tetracyanoethylenes such as tetracyanoethylene (TCNE) and hexacyano-1,3-butadiene; fluorenones such as fluorenone and trinitrofluorenone (TNF); and p-benzoquinones such as p-fluoranyl and dichlorodicyano-p-benzoquinone. Examples of the anions include halogen anions such as Br^-, I^-, Cl^-, I_3^- and Br_2^-; planar type anions such as NO_3^-; tetrahedral type anions such as BF_4^-, ClO_4^- and ReO_4^-; octahedral type anions such as PF_6^-, AsF_6^-, SbF_6^- and TaF_6^-; and metal halogenoid anions such as $Cu(NCS)_2^-$, $Cu(N(CN)_2)X^-$ (wherein X is Br, Cl, etc.), $Cu(N(CN)_2)CN^-$, $Cd(NCS)_2^-$, $Zn(NCS)_2^-$, $Hg(NCS)_2^-$ and $KHg(NCS)_4^-$. Among the above, TCNQ and an iodine anion are preferably used as the electron acceptor.

The organic charge transfer complex of the present invention can be prepared from the above BOPDT-TTF and/or BTPDT-TTF and the above-described electron acceptors by conventional methods such as solution methods, diffusion methods, and methods for preparing a single crystal by electrolytic crystal growth. Further, a method for preparing a complex by heating an electron donor and an electron acceptor in a solution, as described in H. Müller, Synthetic Metals, vol. 39, pp. 261-267 (1990), and a method for preparing fine powder of a complex crystal by ultrasonic treatment.

The organic charge transfer complex of the present invention alone or together with an appropriate binder can be processed into various forms such as powder-compressed sheets, wires, films, membranes, etc. and can be applied to organic electrical conductive materials, organic superconductive materials, organic electrochromic materials, organic electroluminescent materials, etc.

The present invention is now illustrated in greater detail by reference to the following examples which, however, are not to be construed as limiting the invention in any way.

EXAMPLE 1

50 mg (0.12 mmol) of BOPDT-TTF of formula (1) and 24.5 mg (0.12 mmol) of TCNQ as the electron acceptor were weighed and placed in a reaction vessel. The reaction vessel was purged with argon, and 20 ml of chlorobenzene was introduced into the reaction vessel with a syringe. Subsequently, the reaction vessel was heated to a reflux temperature, maintained at that temperature for 10 minutes, and then cooled to room temperature to terminate the reaction. A black precipitate was recovered by filtration, washed with methylene chloride and then pentane and dried under reduced pressure to obtain 58.6 mg (yield: 76%) of the reaction product in the form of powder.

The elemental analysis of the reaction product was made, and the following results were obtained.

Elemental analysis for the reaction product:			
Found:	C, 42.71%;	H, 1.95%;	N, 8.84%

Elemental analysis for (BOPDT-TTF)TCNQ complex:			
Calculated:	C, 42.56%;	H, 1.95%;	N, 9.02%

The found values were well-consistent with the calculated values. Accordingly, it was confirmed that the reaction product was a complex of BOPDT-TTF/TCNQ = 1/1.

The above-obtained (BOPDT-TTF)TCNQ complex was subjected to infrared spectrophotometric analysis. Absorption peaks were found at 2,205 cm^{-1}, 1,560 cm^{-1}, 1,522 cm^{-1}, 1,302 cm^{-1}, 1,046 cm^{-1}, 913 cm^{-1}, 803 cm^{-1}, 675 cm^{-1}, and 468 cm^{-1}. Strong electron absorption vibration was found in the region of from 4,000 to 1,500 cm^{-1}. It was confirmed that a peak ascribed to the stretching vibration of the CN group of TCNQ was shifted from 2224 cm^{-1} to 2204 cm^{-1}, which showed that a partial charge transfer from the donor molecule (BOPDT-TTF) to the acceptor molecule (TCNQ) occurred.

An ESR analysis of the (BOPDT-TTF)TCNQ complex showed a g value of 2.004 and a line width of 7 G, which was close to the g value of free electrons of 2.0029. The spin density was 4×10^{23} spins/mol.

The (BOPDT-TTF)TCNQ complex powder was compression molded into a sheet. The resistance of the sheet was measured by means of a four terminal method. The resistance was 110 $m\Omega cm^{-1}$ (electrical conductivity: 10 S/cm).

For the purpose of comparison, bis(propylenedithio)tetrathiafulvalene (hereinafter referred to as BPDT-TTF) wherein $-CH_2-$ group was introduced in place of the oxygen atom in formula (1) was used to prepare (BPDT-TTF)TCNQ complex in the same manner as above. The sheet prepared from the (BPDT-TTF)TCNQ complex had a resistance of 16 Ωcm (electrical conductivity: 0.06 S/cm). It is clear from these results that the (BOPDT-TTF)TCNQ complex according to the present invention has an improved electrical conductance.

EXAMPLE 2

A chlorobenzene solution containing 71 mg (0.56 mmol) of iodine dissolved therein was added to a solution of 50 mg (0.11 mmol) of BTPDT-TTF of formula (2) in 100 ml of chlorobenzene in an argon atmosphere. The mixture was stirred overnight at room temperature. A black precipitate was collected from the reaction mixture by filtration and washed with carbon tetrachloride to remove residual iodine. The precipitate was dried under reduced pressure to obtain 65 mg (yield: 85%) of the reaction product in the form of powder.

The elemental analysis of the reaction product was made, and the following results were obtained.

Elemental analysis for the reaction product:		
Found:	C, 18.78%,	H, 1.00%

Elemental analysis for $(BTPDT\text{-}TTF)_2I_3$ complex:		
Calculated:	C, 18.66%;	H, 1.25%

The found values were well-consistent with the calculated values. Accordingly, it was confirmed that the reaction product was a complex of BTPDT-TTF/I^- = 2/3.

The above-obtained $(BTPDT\text{-}TTF)_2I_3$ complex was subjected to infrared spectrophotometric analysis. Absorption peaks were found at 1,423 cm^{-1}, 1,364 cm^{-1}, 1,218 cm^{-1}, 1,164 cm^{-1}, 1,124 cm^{-1}, 877 cm^{-1}, 852 cm^{-1}, 810 cm^{-1}, 769 cm^{-1}, 720 cm^{-1}, 517 cm^{-1}, and 478 cm^{-1}.

An ESR analysis of the $(BTPDT\text{-}TTF)_2I_3$ showed a g value of 1.9958, a line width of 180 G, and a spin density of 1.49×10^{23} spins/mol.

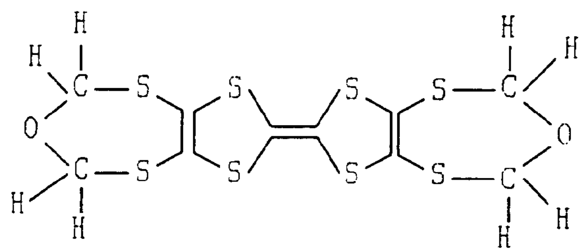
The electrical conductance of the $(BTPDT\text{-}TTF)_2I_3$ complex was 2.4×10^{-7} S/cm on the level of semiconductor.

As described above, the organic charge transfer complex of the present invention has low anisotropy and high conductivity in comparison with conventional tetrathiafulvalene complexes, and it can be expected that the organic charge transfer complex of the present invention can be applied to superconductive materials having a high critical temperature, conductive materials having a wide range of electrical conductivity ranging from semiconductors to metallic materials, magnetic substances, electrochromic materials, and electroluminescent materials. Accordingly, it can be highly expected that the organic charge transfer complex of the present invention can be applied to various wiring materials, wires, printed circuits, sensors, elements, shielding materials, reflective materials, photoconductive materials, and magnetic materials.

While the present invention has been described in detail and with reference to specific embodiments thereof, it is apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and the scope of the present invention.

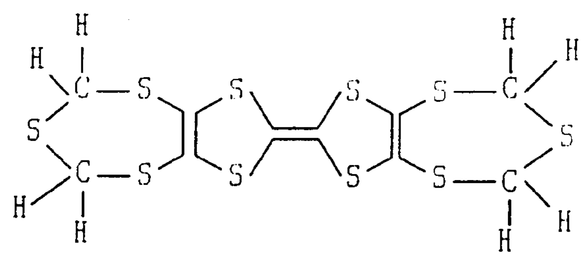
Claims

1. An organic charge transfer complex comprising an electron donor and an electron acceptor, said electron donor is at least one of bis(oxapropylenedithio)tetrathiafulvalene represented by formula (1):



(1)

and bis(thiapropylenedithio)tetrathiafulvalene represented by formula (2):



(2)

2. An organic charge transfer complex as claimed in claim 1, wherein said electron acceptor is at least one of tetracyanoquinodimethane and an iodine anion.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 10 2168

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	SYNTHETIC METALS vol. 42, no. 1-2 , 1991 , AMSTERDAM NL pages 1963 - 1970 R. P. SHIBAEVA ET AL 'New cation-radical salts based on BEDT-TTF analogs with polyhalide anions' * page 1963 - page 1965 * ---	1	C07D519/00 H01B1/12
X	SYNTHETIC METALS vol. 42, no. 3 , 1991 , AMSTERDAM NL pages 2409 - 2413 H. NAKANO ET AL 'Synthesis of multi-chalcogen TTF-derivatives and electrical conductivities of their radical-ion salts' * page 2409 - page 2411; table 2 * ---	1,2	
X	CHEMISTRY LETTERS. no. 11 , 1990 , TOKYO JP pages 2129 - 2132 H. NAKANO ET AL 'Synthesis of 4,5-ethylene dithio-4'5'-(2-oxatrimethylenedithio)-tetrathiafulvalene (EOTT) and electrical conductivities of their ion-radical salts' * page 2130; table 1 * ---	1	TECHNICAL FIELDS SEARCHED (Int.Cl.5) C07D H01B
X	JOURNAL OF MOLECULAR ELECTRONICS vol. 5, no. 1 , 1989 , CHICHESTER GB pages 33 - 36 V. KHODORKOVSKY ET AL 'Electron-donating ability of tetrathiafulvalene derivatives invedtigated by cyclic voltammetry' * page 33 - page 34; table 1 * --- -/--	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24 May 1994	Voyiazoglou, D

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
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D : document cited in the application
L : document cited for other reasons

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EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	CHEMICAL ABSTRACTS, vol. 111, no. 13, 25 September 1989, Columbus, Ohio, US; abstract no. 115150b, R. MEDNE ET AL 'Synthesis and crystal structure of bis(oxapropylenedithio)tetrathiafulvalene hexyfluorophosphate' page 661 ; * abstract * & IZV. AKAD. NAUK SSSR, SER. KHIM. no. 1 , 1989 pages 174 - 176 ---	1	
P,X	BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN vol. 66, no. 6 , June 1993 , TOKYO JP pages 1773 - 1777 H. MÜLLER ET AL 'Synthesis and properties of bis(oxybid(methylenethio)tetrathiafulvalene and its sulfur analog: pi-donors for organic metals' * page 1773 - page 1775 * -----	1,2	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)

The present search report has been drawn up for all claims

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THE HAGUE	24 May 1994	Voyiazoglou, D

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